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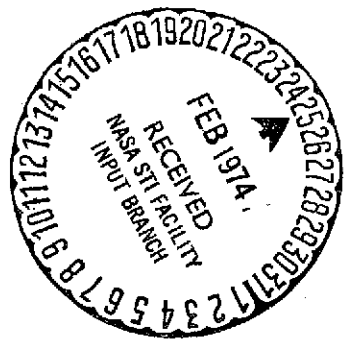

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16. Abstract

The kinetics of oxide films in titanium is studied experimentally, using tempering colors as an indicator of the film thickness during the dissolution process. It is found that dissolution proceeds faster in vacuum than under normal conditions. Tests with welded joints showed that the presence of oxide films of a thickness ranging between 25 and 540 A at the butt surfaces does not impair the welding process, and that the weld attains the tensile strength of the matrix metal after one hour at a process temperature of 900°C.

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INVESTIGATION OF THE DISSOLUTION PROCESS OF OXIDE FILMS IN TITANIUM

V. V. Peshkov and E. S. Vorontsov

The kinetic mechanisms of growth of oxide films on metals, /99* including titanium, have been studied quite well [1-3]. Oxidation of titanium can be considered to be a process of absorption of oxygen by the metallic base and the formation of an oxide film. The overall oxidation rate, of which the amount of oxygen consumed in a unit time can be considered a measure, equals the sum of its consumption rates in dissolution (v_1) and in formation of a rutile film (v_2)

$$v = v_1 + v_2 \qquad (1)$$

The effect of pressure on the rate of growth of the film has been studied very little, and it remains an open question, as to the conditions under which dissolution of the oxide layer in the base, i.e., cleansing the oxide from the titanium surface, can be accomplished. This question is of definite, not only theoretical, but practical interest, since cleansing the surfaces of titanium parts accompanies diffusion welding and other processing operations of them.

To investigate the kinetics of dissolution of the oxide film in titanium, we used the interference indicator method [4-7]. Since the color of the film is a function of its thickness, during oxidation of the metal and thickening of the oxide layer, the coloring changes in the sequence: yellow → brown → violet → blue, and during dissolution of the film in the base, in the reverse sequence. Therefore, dissolution of oxygen should be detected

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* Numbers in the margin indicate pagination in the foreign text.

visually by the colored film in titanium, with decrease in its thickness. In this case, the tempering color can play the part of process indicator.

Samples of technically pure VT-1 titanium and OT4 titanium alloy, 25 × 25 × 0.3 mm in size, were polished to surface finish class ∇6, rinsed in ethyl alcohol and oxidized in air at 600°C for a period of 15 min, until appearance of a light blue film (∿540 Å) [3], which was adopted as the standard.

The oxidized samples were placed in a container, made of OT4 titanium alloy and having two chambers I and II (Fig. 1). The container was closed with membrane 6, which was seamed with airtight seam 7 by argon arc welding. Chambers I and II were connected to a VN-2MG vacuum pump through tube 2. The pump maintained a residual pressure of $2 \cdot 10^{-2}$ mm Hg at the outlet of the main vacuum line during the entire test. The pressure drop across the membrane pressed it to the container seal, cutting off the chamber II and creating conditions in it for autoevacuation, similar to those which arise in closed chambers during diffusion welding, owing to the roughness of the parts being joined.

During the test, the container with samples was placed in a furnace with a neutral medium, which could be heated to a specific temperature, and held there for a fixed period of time. Sample temperature was measured with a chromel-alumel thermocouple, the hot junction of which was attached to the container. After holding the container isothermally, it was removed from the furnace and quickly cooled in air, without cutting off the pump. The conclusion as to change in its thickness was drawn from the change in color of the film (Table) [3].

Part of the tests were carried out in a vacuum chamber, in which the pressure was held at $2 \cdot 10^{-2}$ mm Hg during the entire period of isothermal annealing.

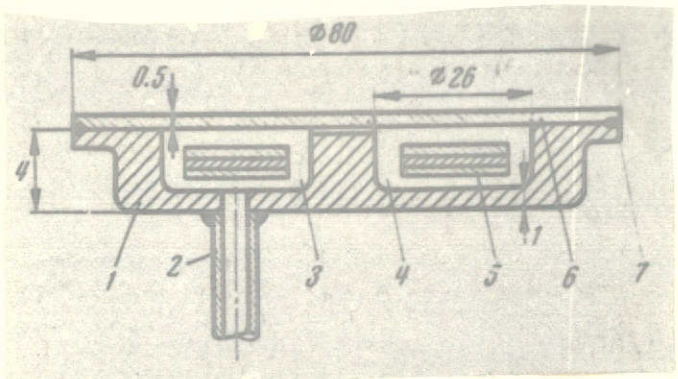

Fig. 1. Container for isothermal annealing of samples: 1. housing; 2. tube; 3. chamber I; 4. chamber II; 5. samples; 6. membrane; 7. seam.

In a series of tests to investigate the effect of oxide films on the strength of the welded joint of OT4 alloy samples, formed by diffusion welding at various temperatures, samples 16 mm in diameter and 30 mm long were used. The surfaces to be welded were turned on a lathe to a degree of surface finish ∇6, and an oxide film ∿540 Å thick was then applied to one of the samples being welded. Welding of the samples was carried out in a vacuum of $2 \cdot 10^{-2}$ mm Hg, with a contact pressure of 0.1 kg/mm^2, for a period of 60 min at various temperatures. After welding, standard Gagarin samples were prepared and tested on a tensile testing machine.

As a result of the tests carried out, quantitative relationships of change in thickness of a standard sample (∿540 Å) to /100

THICKNESS OF INTERFERENCE COLORED OXIDE FILMS ON TITANIUM (I ORDER SPECTRUM)

Sample color	y, Å	Sample color	y, Å
Light azure	542	Light brown	438
Azure	536	Yellow-brown	434
Blue	515	Dark yellow	358
Blue-violet	510	Yellow	349
Violet	492	Light yellow	343
Brownish violet	456	Pale yellow	340
Brown	447	Yellowish	330

time were obtained, in the 500-700°C temperature range, at a pressure of $2 \cdot 10^{-2}$ mm Hg and under autoevacuation conditions (Fig. 2).

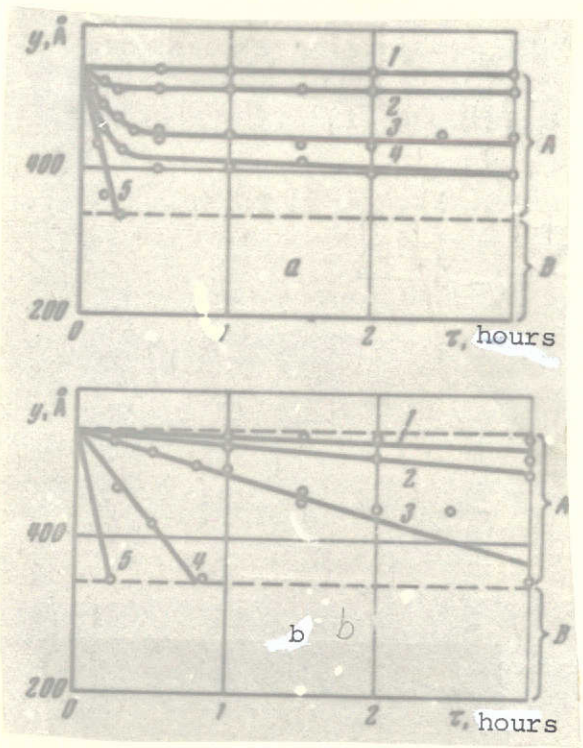

Fig. 2. Change in thickness of oxide film on titanium, while holding samples at pressure of $2 \cdot 10^{-2}$ mm Hg (a) and under autoevacuation conditions (b), at various temperatures: a) 1. 600°C; 2. 625°C; 3. 650°C; 4. 675°C; 5. 700°C; b) 1. 525°C; 2. 550°C; 3, 575°C; 4. 600°C; 5. 625°C; A. film color range; B. colorless film range.

At a pressure of $2 \cdot 10^{-2}$ mm Hg, discoloration of the film proceeds less effectively than under autoevacuation, i.e., under conditions of absorption of oxygen by the walls of sealed chamber B. At 650°C, a 3-hour exposure leads to decrease in the thickness of the film by 95-100 Å. Increasing the temperature to 700°C leads to discoloration of the film in 12-15 min. This picture can be explained by the ratio of the rates of growth and dissolution of the film. The rate of growth of the film is a function of its thickness, and it proves to be higher, the thicker the film [1, 3]. Reduction in film thickness in the initial stage is evidence that the rate of its dissolution by the base becomes higher than the rate of growth of the oxide layer. These rates equalize in proportion to dissolution of the film. The thickness of the tarnish layer stabilizes.

At temperatures of 700°C and higher, the difference in rates of dissolution and growth of the oxide layer apparently is so great that decrease in film thickness cannot increase its growth rate to such an extent that the solution of oxygen in the metal base is compensated for.

Autoevacuation reduces the rate of growth of the films so much that complete decolorization of it in 15 min at 625°C is possible. Under these conditions, the film thickness decrease over time is linear, at least in the 500-625°C temperature range investigated. Here, the average rate of the process ($\bar{v}$) becomes equal to the true rate (v), i.e.

$$\frac{dy}{d\tau} = \frac{\Delta y}{\tau} = ke^{-\frac{E}{RT}} \qquad (2)$$

where y is the film thickness, τ the time, k a preexponential factor, E the apparent activation energy and T the absolute temperature.

With change in coloration of the film within the limits of the two standard colors, Δy = const and, then,

$$\log \tau = \frac{E}{2.3\,RT} + C \qquad (3)$$

where $C = \log \Delta y - \log k$, i.e., τ and E become the primary kinetic /101 characteristics. Calculation of the apparent activation energy E by equation (3), using the data presented in Fig. 2 b, gives a value of about 75,000 kcal/mole.

The change in film thickness, calculated by equation (2), after 1 hour of isothermal exposure in the 500-725°C range, at a pressure of $2 \cdot 10^{-2}$ mm Hg, and under autoevacuation conditions,

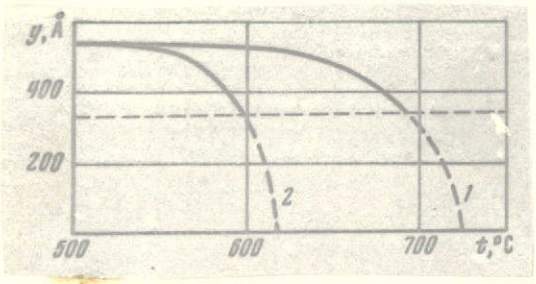

Fig. 3. Change in thickness of oxide film on titanium at different temperatures (1 hour exposure): 1. pressure $2 \cdot 10^{-2}$ mm Hg; 2. autoevacuation.

is shown in Fig. 3. In this way, the results of the tests carried out give a conception of the time for cleansing the oxide film from the titanium surface.

Since the colorless film has a thickness changing from 0 to 320 Å, it is extremely difficult in practice to investigate the effect of its presence on strength of a welded joint at various temperatures -- the film thickness proves to be indefinite.

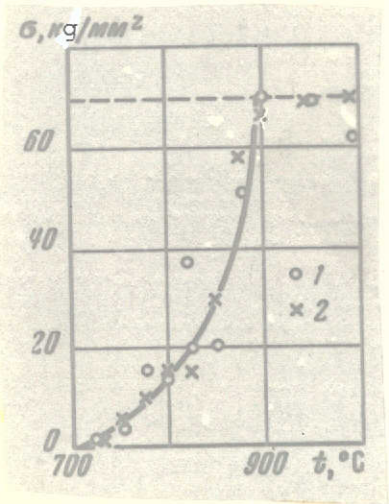

Fig. 4. Strength of titanium specimen joint vs. welding temperature: 1. samples with ∿25 Å film, existing after mechanical treatment; 2. samples, to one of welded surfaces of which an oxide film ∿540 Å thick has been applied.

The results of tensile strength testing of samples, welded with previously applied oxide films of standard coloration -- light azure (∿540 Å) and colorless (∿25 Å) -- are presented in Fig. 4. They show that, even in the presence of an oxide film about 600 Å thick in the joint of the two welded parts, the strength of the welded joint practically does not differ from the strength of joints produced by welding of similar specimens, but with a 25 Å film existing after mechanical treatment.

Conclusions /102

1. Interference coloration of oxide films on titanium can serve as an indicator during investigation of the process of their dissolution in a metallic base. In this case, dissolution of films of various thicknesses can be investigated over a broad range of temperatures and pressures.

2. The process of dissolution of films of standard coloration in the I order spectrum, at a pressure of $2 \cdot 10^{-2}$ mm Hg and under autoevacuation conditions, i.e., in a closed chamber of titanium alloy, was studied by the interference indicator method. In this case, it was found that dissolution of the film under autoevacuation conditions proceeds faster than at the specified vacuums used in the tests.

3. Strength of welded samples, having oxide films 25 and 540 Å thick on the butt surfaces, was tested. It was found that the presence of an oxide film in the butt, even with a thickness of about 600 Å, does not prevent welding and, at a process temperature of about 900°C, the tensile strength of the welded joint reaches the strength of the matrix metal in 1 hour.

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